PRODUCTS FROM TWO-STEP COAL LIQUEFACTION USING THREE DIFFERENT FIRST-STEP REACTOR PACKINGS

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INTRODUCTION

In the current work, laboratory-scale batch and flow studies have been conducted with various nominally non-catalytic materials as reactor packing for the first-step of a two-step coal hydroliquefaction process being studied at the Morgantown Energy Research Center's Liquid Fuels Research and Development Branch. An examination of the available literature on some three dozen coal liquefaction processes gave no evidence for any previous studies along these lines. Several of the processes have been compared in review articles (1, 2).

The process studied is a two-step coal/recycle oil slurry-feed hydroliquefaction process, with removal of solid residue between the two steps, in which the second-step catalytic reactor is preceded by a first-step reactor containing a nominally non-catalytic material selected for its ability to induce desirable hydropyrolytic reactions. These reactions are principally the conversion of asphaltene intermediates from the coal feed to oils and/or to asphaltenes of higher hydrogen content. Unconverted asphaltenes will likely result in coke formation in the catalytic reactor, greatly reducing catalyst activity and selectivity. Hydropyrolytic treatment (thermally induced dissociation or disproportionation of hydrogen) of petroleum residues, before a catalytic desulfurization, is designed to break down the less thermally stable asphaltic compounds so as to give less coke formation on the desulfurization catalyst (3). The presence of a high surface area carbonaceous material apparently accelerates the desired reactions, as in the "Combifining" process in which asphaltic compounds are treated with hydrogen at 30 atm in a fluidized-bed of petroleum coke at 380-410° C (4). The deactivation effect of coal asphaltenes is reduced by hydropyrolytic splitting on the surface of semi-coke dust (5). Pore diameters between 100 and 1,000 ångstroms, and larger, appear necessary to allow free access of asphaltenes for their conversion. Conversely, when only small diameter pores are present, asphaltenes are reported to block the pores and the material is rapidly deactivated (6).

The material desired as first-step reactor packing for the process studies must, therefore, in consideration of the pertinent literature, have a moderate surface area with a surface structure allowing or promoting carbon deposition, high porosity, and large pores (0.1 micron, or larger). A nominally non-catalytic material is indicated, to restrict surface reactions to those induced by a carbonaceous deposit. This would appear to rule out silica-alumina and possibly gamma-alumina, while allowing alpha-alumina and silica. Vitrified ceramics would apparently not offer sufficient surface area or porosity, although they are nominally non-catalytic for this reason.

Dissolution of the coal in the first-step reactors allows separation of the mineral residues. Although coal minerals have been suspected to have substantial coal-liquefaction catalytic behavior (7), these same minerals, or trace metals in them, act as strong poisons for hydrogenation catalysts (8). In addition, the sub-micron, clay-derived mineral residues plug the pores of

the catalyst. Massive plugging between catalyst pellets occurs when the mineral residues settle out. In the initial developmental work on the Synthoil Process for making low-sulfur fuel oil from coal it was demonstrated that this type of plugging could be prevented by a highly turbulent flow of hydrogen through the catalyst bed (9). However, if the density of the product oil is reduced from that of a fuel oil to that of a kerosine and gasoline rich product, massive plugging occurs even with highly turbulent hydrogen flow, because the light kerosine and gasoline flash off into the gas phase, leaving insufficient liquid vehicle to carry residual solids through the fixed bed.

By introducing an effective hydropyrolytic step followed by separation of the mineral matter, the catalyst, such as the widely used cobalt molybdate catalysts on silica-promoted alumina supports, can have a longer life, and can be used at the milder temperatures and pressures for which they were designed, rather than at more rigorous conditions necessary for trying to maintain some degree of activity.

With regard to pressure, as the hydrogen pressure increases, there is a maximum in the overall yield of hydrocracking product (10). In a two-step coal hydrocarbonization-tar vapor catalytic hydrogenation laboratory-scale study, the maximum yield of product was obtained at a hydrogen pressure of 40 atm (11). With an increase in temperature above 400° C, thermal splitting by a free radical mechanism starts to be significant, leading to the formation of coke-like materials. High hydrogen pressures will reduce coking to some extent, but are economically unfavorable, while resulting in decreased yield of liquid product. At 375°-400° C and 1,500 psig, catalytic hydrogenation of a low-temperature coal tar gave a product with high aliphatic character and a high diesel index (12).

EXPERIMENTAL

Stirred Batch Reactor Runs

Coal-oil slurries were made up with one part by weight of run of mine coal (Pittsburgh No. 8 seam, Ireland mine, 33.06 weight percent volatile matter, 0.72 weight percent moisture, 19.51 weight percent high-temperature ash, carbon 60.42, hydrogen 4.32, nitrogen 0.92, oxygen 7.96, and sulfur 4.62 weight percent, all by analysis) and two parts of hydrogenated Reilly tar oil. This hydrogenated oil was prepared in a one-gallon stirred batch reactor with hydrogen gas at 390° C and 1,800 psig for three hours, using about 1,800 ml oil and about 32 g presulfided cobalt molybdate on silica-promoted alumina 1/8-inch pellets (Harshaw CoMo-0402T 1/8") in two baskets attached to the stirrer, as shown in figure 1. The catalyst was presulfided in situ with a flow of 10-15 percent hydrogen sulfide in hydrogen at 3-4 liters per hour per 100 g catalyst for 1.5 hours at 400° C and atmospheric pressure. Gas chromatographic/mass spectrometric analysis showed about 20 percent identifiable hydroaromatics, or hydrogen donors, in the hydrogenated oil, compared to none in the original oil. The identities of these are discussed under Results.

These coal/oil slurries were examined for their behavior over two different kinds of packing that could be tried in the first-step reactor of the two-step process. These were a vitrified ceramic (Norton "Denstone 57" catalyst bed support,[1/] consisting of 1/4-inch balls having a silica content of 56.4 weight percent, with a surface area of about 0.01 m^2/g and a very low porosity),

1/ Use of trade names or company names is for identification only and does not imply endorsement by ERDA.

and alpha-alumina (Girdler catalyst carrier T-375, consisting of 1/8-inch pellets having a silica content of only 0.02 weight percent, with a surface area of about 5.3 m^2/g, and 0.06-0.8 micron pores). A series of runs was made in a one-gallon stirred batch reactor, using 36.15 g of "Denstone" or alpha-alumina in two baskets attached to the stirrer, and about 900 g slurry at 450° C and 1,800 psig for three hours, or about 1,800 g slurry at 430° C and 1,500 psig for three hours, the reactor being brought up to the desired pressure with hydrogen gas. Air was flushed from the system with nitrogen gas and nitrogen purged from the system with hydrogen gas before partial pressurizing, heating, and then any final pressurizing. As hydrogen was consumed the pressure was maintained with additional hydrogen.

Half of each first-step product from all runs was filtered to remove mineral residue, and the filtered and unfiltered portions were then hydrogenated over the same catalyst used to prepare the hydrogenated tar oil (Harshaw CoMo-0402T 1/8"). The second-step run conditions for all eight runs were identical, namely, 1,500 psig (achieved with hydrogen gas) at 380° C for one hour in a one-gallon stirred reactor, using about 200 g feed and 0.4 g presulfided cobalt molybdate on silica-promoted alumina in two baskets attached to the stirrer. The quantity of catalyst was chosen to approximate 500 hours operation at a liquid hourly space velocity of one in a fixed bed process.

The products were analyzed by 1) solvent extraction to recover benzene insolubles, asphaltenes (benzene-soluble, cyclohexane-insoluble), and oils (cyclohexane-soluble); 2) liquid elution chromatography of the oils from activated alumina with cyclohexane and benzene (to remove colored resins); 3) gas chromatographic mass spectrometric analysis of the cleaned oil to identify and quantify individual compounds; 4) elemental analysis for determination of the atomic hydrogen-to-carbon ratio in various samples; 5) gas chromatographic analysis of the gaseous products for the amounts of the individual hydrocarbons; and 6) physical property determinations (density and distillation curves) on the filtered products. Differences due to different operators, procedures, or equipment were avoided. The separation procedures were similar to those previously used for analysis of low-temperature coal tars (13).

0.2 Pounds Coal/Hour Flow System

A schematic flow diagram of this system is detailed in figure 2. Interchangeable reactors packed for either first-step runs, or with catalyst for second-step runs, were used in the clam shell heaters. This laboratory-scale equipment was used in a run of nearly 48 hours duration to prepare about five gallons of hydrogenated tar oil for slurry preparation. The Reilly tar oil was fed at a rate of about 375 ml/hr (LHSV=1.4) through presulfided cobalt molybdate on silica-promoted alumina at 380° C and 1,500 psig hydrogen. Product sample collected at 44 hours analyzed for 26.26 weight percent hydroaromatics, while the hydrogen donor content for the composite five gallon product was 26.88 weight percent, showing no significant decline in catalyst activity over about 48 hours operation. The tar oil feed contained no hydrogen donors.

Hydropyrolytic first-step runs were made in the same reactor (1-inch, schedule 80, 304 stainless steel pipe), with the first seven inches packed with 1/2-inch lengths of 1/4-inch O.D. 304 stainless steel tubing and the remaining 21 inches packed with either 1/8-inch alpha-alumina pellets, or a 99.5 weight percent alpha-quartz packing (Girdler catalyst carrier T-1571, consisting of 3/16-inch silica spheres with a surface area of about 131 m^2/g, and 1-18 micron pores). The total volume of the reactor was 270 ml. The slurry feed was made

from one part by weight of 70 percent minus 200 mesh, 100 percent minus 100 mesh, Ireland Mine coal (Pittsburgh No. 8 seam), and three parts of the hydrogenated Reilly tar oil, made as described above. The slurry was fed at a rate between 245 and 375 g/hr at 440° C, 1,500 psig, and a hydrogen flow rate of about 7.0 scfh. Total run time with each first-step packing was nearly 16 hours. The faster feed rate for the bed packed with spheres compensated for the larger void volume for the spheres.

The products from both runs were filtered to remove mineral residue, and the residue washed with benzene to remove adhering oil, dried, and weighed. The filtered products were then subjected to catalytic hydrogenation in the second-step reactor under conditions essentially the same as those used to prepare the hydrogenated tar oil. The second-step reactor was identical to the first-step reactor, except for the packing, which was entirely sulfided cobalt molybdate on silica-promoted alumina. The liquid feed was introduced at a rate between 250 and 350 g/hr at 380° C, 1,500 psig, and a hydrogen flow rate of about 7.0 scfh. Total run time was up to about 11 hours.

RESULTS AND DISCUSSION

Stirred Batch Reactor Runs

Mass, hydrogen, and carbon balances for the stirred batch reactor runs, including data on the four first-step runs and the four corresponding second-step runs with unfiltered first-step product as feed, are presented in tables 1 through 3. The process conditions for all stirred batch reactor runs are summarized in table 4.

Mass balances varied between 90.4 and 99.6 percent, with an average of 96.7 percent. Six of the eight runs had mass balances between 97.7 and 99.6 percent. Ammonia, hydrogen sulfide, and water were determined by calculating the decrease in elemental nitrogen, sulfur, and oxygen in going from solids and liquids in the feed to those in the product, and converting to the equivalent weights of the three compounds. Essentially all the water, and nearly all of the hydrogen sulfide, were evolved in the first-step runs. The alpha-alumina appeared to favor a greater production of water and hydrogen sulfide than the Denstone vitrified ceramic, except for hydrogen sulfide at the more rigorous conditions.

Hydrogen balances varied between 93.5 and 108.6 percent, with five of the eight runs between 98.7 and 103.8 percent. Hydrogen usage was estimated from the pressure gauges on the cylinder regulators, but temperature variations restricted the accuracy of this approach because the cylinders were mounted outside the high pressure cell building. A better estimate of hydrogen usage was obtained by assuming a balance of 100 percent and correcting the grams H_2 gas in, accordingly. The gas chromatographic analyses of product gases showed that the alpha-alumina favored a greater production of hydrocarbon gases than the Denstone vitrified ceramic. This coupled with the greater production of H_2O and H_2S would be expected to require a greater consumption of hydrogen with alpha-alumina. The corrected values for grams H_2 gas in come much closer to showing this than the uncorrected values, which appear to be generally unreliable.

Carbon balances varied between 90.5 and 106.9 percent, with half the values between 97.1 and 106 percent. The amounts of CO and CO_2 in the product gases from the first-step runs appeared to be somewhat high compared to the previous work, and may account for the 104.5 to 106.9 percent carbon recoveries for the first-step runs, as opposed to the 90.5 to 99 percent recoveries for the second-step runs.

The mass, hydrogen, and carbon balances for the stirred batch reactor runs fall within the range of values generally found for such laboratory-scale operations.

The results of the solvent extraction analysis of the products from the stirred batch reactor runs are summarized for all eight runs in table 4, with the data for the paired "Denstone" and alpha-alumina first-step reactor materials placed together for ease of comparison. A large, but noncalculable, part of the oils comes directly from the compounds in the oil used to make the coal/oil slurry, while the rest of the oil comes from hydroliquefaction of the coal and the asphaltic constituents. Assuming that the lowest oil yield from the coal was only about one percent, with almost 90 percent recovery of vehicle oil (10 percent conversion to gas and light oils), it can be seen that in most instances the amount of oils was increased from 20 percent to as much as three-fold by using alpha-alumina instead of vitrified ceramic. In one instance, even though the oil yields were essentially the same, the atomic hydrogen-to-carbon ratio for the alpha-alumina-derived oil was much higher, as shown later, demonstrating a higher total hydrogen gain for the alpha-alumina-derived oil.

In line with the larger amounts of coal-derived oil, using the alpha-alumina, larger amounts of identifiable coal-derived compounds were obtained (table 5), with the compounds arranged according to increasing boiling point. These six compounds are all polycyclic aromatic hydrocarbons which were not detectable in the hydrogenated tar oil, and therefore probably came from the coal via the asphaltenes. The slightly lower concentration at the higher temperature and pressure may be explained by the dilution with a little more of other coal-derived compounds. There was about 50 or 60 percent more coal-derived, or more correctly, asphaltene-derived compounds in the second-step product oil using first-step product from the alpha-alumina bed as feed. Possibly this is because this feed did not deactivate the cobalt molybdate catalyst as much as the first-step product from the vitrified ceramic.

The higher activity of alpha-alumina for producing low-boiling hydrocarbons directly from coal or asphaltenes was also demonstrated by the gaseous hydrocarbons collected during the first-step runs. The volume of methane, ethane, propane, and butanes per pound of coal was in each instance greater for each hydrocarbon compound when using alpha-alumina (table 6). The yields of hydrocarbon gas are also greater at 450° C than at 430° C, because this is the temperature range in which bituminous coals show a rapid increase in thermal decomposition. The greater yields of hydrocarbon gas with alpha-alumina are not due to increased dealkylation of alkylated polycyclics in the oil (table 5). In face, somewhat greater yields of alkylated compounds were obtained at both operating temperatures, using alpha-alumina.

The yields of asphaltenes (table 4) were less with alpha-alumina, generally down to about one-half the quantity obtained with the vitrified ceramic. In the one instance in which the yields were close, the atomic hydrogen-to-carbon ratio was substantially higher for the alpha-alumina-derived asphaltene (table 7). Under both of the first-step run conditions the atomic hydrogen-to-carbon ratios for the asphaltenes were clearly higher using alpha-alumina, as shown in table 7. In one instance, the oil derived in the presence of alpha-alumina was distinctly higher in atomic H/C. In the other, the two oils had nearly identical values of atomic H/C. The yield of oil in the latter was greater with alpha-alumina (table 4), demonstrating a higher total hydrogen uptake.

The total amounts of nine important classes of alkylated polycyclic aromatics were greater for the products obtained using alpha-alumina (table 5), under both first-step run conditions. Larger amounts were obtained with both

first-step materials at the more rigorous conditions, due to more reaction of the coal, and the percent increase for alpha-alumina was considerably greater.

The identities and amounts of the eight identifiable hydroaromatics, or hydrogen donors, in the hydrogenated tar oil used to make up the slurry for the stirred batch reactor runs are shown in table 8. Analysis of the oil in the two different first-step products showed nearly double the consumption of hydrogen donors in the presence of alpha-alumina, compared to the vitrified ceramic.

It is possible that the much greater surface area and pore volume of the alpha-alumina compared to the vitrified ceramic could offer more carbonaceous surface for the hydrogen donors to react. Examination of the spent materials visually, and by scanning electron microscopy, showed that a black, carbonaceous deposit covered the exterior of the ceramic balls, but extended throughout the interior of the alpha-alumina pellets.

In all instances, the presence of mineral residue in the second-step reactor gave improved results (table 4) as regards decreased yields of asphaltenes and increased yields of oils. As mentioned in the Introduction, this apparent advantage is outweighed by several serious disadvantages.

Because the slurry feed to the stirred batch reactor runs was 67 percent by weight of hydrogenated tar oil, the distillation curves to a final boiling point of 495° C of the first-step products and the vehicle oils were rather similar. However, some differences were evident which reflected the differences in activity of the two different reactor packings and the two different reactor conditions, as shown in table 9. The largest cut, the median boiling diesel oil fraction, was essentially identical for the two tar oils and three of the four products. The fourth product, obtained with the alpha-alumina packing under the rigorous conditions, showed a substantial decrease in this major fraction, with a corresponding substantial increase in the lowest molecular weight fraction, the gasoline cut. At the milder conditions, there was only a little more gasoline range fraction with the alpha-alumina packing than with the vitrified ceramic packing, and as expected both packings gave substantially less gasoline cut than under the more rigorous conditions.

0.2 Pounds Coal/Hour Flow System

The process conditions for all flow reactor runs, the results of the first-step product filtration, the solvent extraction analysis, and the product gas analysis are summarized for all four runs in table 10. The residue filtered off from the first-step products, after washing with benzene to remove adsorbed oil, essentially equalled the calculated mineral matter in the coal feed, demonstrating essentially complete dissolution of the organic part of the coal. The benzene insolubles in the filtered product from the silica balls was more than twice that from the alpha-alumina pellets.

The total yield of total hydrocarbon gases from the alpha-alumina bed reactor was nearly four times that from the silica bed reactor. Conversely, there was a nearly fourfold greater yield of hydrocarbon gases from the catalytic reactor, using the silica bed product as feed. Thus, most of the hydrocracking to give gas occurs in the alpha-alumina bed, where the concomitant carbon deposit formation does little harm, whereas a little over half of the gas formation occurs in the catalytic bed used after the silica bed, where carbon deposits are undesirable. The conversion of benzene insolubles to asphaltenes in this catalytic bed may be undesirable for similar reasons. The residence time for the liquid phase in the first-step reactor was estimated to be less than 20

minutes, compared to a residence time (not the time of contact with the packing in the baskets) of three hours in the stirred batch reactor. This probably explains the considerably lower yield of hydrocarbon gases in the flow system compared to the batch system.

In line with the larger amounts of coal-derived oil from the alpha-alumina bed, compared to the silica bed, somewhat larger amounts of identifiable coal-derived compounds were also obtained in the first-step product, as shown in table 11, with the compounds arranged according to increasing boiling point. The alkylated compounds in the first-step product from alpha-alumina were about the same as those from silica. Thus, the greater yields of hydrocarbon gas with alpha-alumina are not due to increased dealkylation. It should be noted that some of the compounds identified were both coal-derived and alkylated.

The identities and amounts of the ten identifiable hydroaromatics, or hydrogen donors, in the hydrogenated tar oil used to make up the slurry for the flow system are shown in table 8. There was a substantially greater consumption of hydrogen donors in the alpha-alumina bed than in the silica bed, in line with the better quality first-step product from the alpha-alumina. The proportion of hydrogen donors consumed in the flow system alpha-alumina first-step run was actually greater than that in the corresponding batch system first-step run because of the higher ratio of tar oil to coal in the flow system, as well as the higher initial concentration of hydrogen donors.

Examination of the used first-step packings showed a much greater degree of carbon deposition on the alpha-alumina than on the silica. Even though the silica packing had a much greater surface area, all of the analytical results on the products indicated greater activity with the alpha-alumina. The structure of the alpha-alumina surface may be such as to allow or promote the type of carbonaceous deposit promoting the desired hydropyrolytic reactions of the coal/hydrogenated tar oil slurry.

Scanning electron microscopy showed random stacks of flat crystallites of carbon. It is suggested that the carbon level reaches an equilibrium due to reduction by hydrogen, and physical attrition. Small amounts of carbonaceous material were found in the benzene-washed residue from filtration of the first-step products.

The filtered first-step product from the flow system using alpha-alumina packing at 1,500 psig and 440° C had an appreciably lower density than the corresponding product using silica packing (table 12). This was not due to less coal dissolved (table 10), but probably was because of the smaller amounts of benzene insolubles and asphaltenes in the product. As shown in table 12, the filtered first-step product from the batch system using alpha-alumina packing at 1,500 psig and 430° C also had an appreciably lower density than the corresponding product using Denstone vitrified ceramic. For both the batch and flow systems the density increase of the product over that of the slurry vehicle oil was only about half as great for alpha-alumina as for the silica, or Denstone.

Because the first-step reactor did not contain any material capable of catalyzing extensive hydrodesulfurization or hydrodenitrification reactions, the filtered first-step products from both the batch and flow systems, with vitrified ceramic, silica, and alpha-alumina packings, all showed retention of heteroatoms (table 13). There was essentially no reduction in nitrogen content. Identifiable nitrogen compounds included pyridines, quinolines, and carbazoles. Alpha-alumina packing in the batch system was slightly better than the vitrified ceramic for reduction of heteroatoms, and this, along with the much greater yield of hydrocarbon gases and oils, required a much greater consumption of

hydrogen from hydroaromatics. Thus, in the first-step product from the alpha-alumina bed there was a little less hydrogen because of loss as hydrogen sulfide, ammonia, water, hydrocarbon gases, and volatile light oils. Silica packing was slightly better than alpha-alumina for reduction of heteroatoms in the flow system, but much inferior for the production of hydrocarbon gases and oils, so that the alpha-alumina product showed a greater consumption of hydrogen donors, and a slight lowering of hydrogen content thereby.

Conversely, the alpha-alumina bed first-step product, when processed at 1,500 psig hydrogen and 380° C in the second-step cobalt molybdate bed, gave a second-step product with fewer heteroatoms, a higher hydrogen content and a higher atomic hydrogen to carbon ratio than that from the first-step product from the silica bed (table 14). The second-step catalyst was more active in converting first-step product from the alpha-alumina bed. A greater second-step gas yield (table 10) with its concomitant greater carbon deposition on the catalyst was observed in converting first-step product from the silica bed. The second-step product, starting with alpha-alumina for first-step packing, had three times the increase in hydrogen content, and atomic H/C, and three times the decrease in nitrogen content as compared to the second-step product starting with silica for first-step packing.

CONCLUSIONS

In the two-step coal hydroliquefaction process studied there were large differences in the behavior between various first-step nominally non-catalytic reactor packings. These results may be due to differences in the ability of the packing surface to promote or allow a sufficient amount of the type of carbonaceous deposit on which desired hydropyrolytic conversions of coal and/or asphaltenes molecules could occur by interaction with hydrogen donors (and hydrogen). The preferred packing produced asphaltenes with higher atomic H/C ratios and/or increased conversion to oils. These products appeared less likely to deactivate the cobalt molybdate catalyst used in the second-step reactor. The greater activity of the catalyst was indicated by the production of a second-step product with lower heteroatom content and higher atomic H/C, with negligible hydrocarbon gas formation and concomitant carbon deposition.

The preferred first-step packing was shown to be a moderate surface area, large pore size, very low silica content alpha-alumina. A high surface area, large pore size, pure silica, and a very low surface area, negligible porosity vitrified ceramic were less effective. The chemical as well as the surface properties of the packing appeared to affect performance. The alpha-alumina produced more first-step hydrocarbon gas, without increasing dealkylation, giving more first-step light oil, more total oil of a lower density, and less asphaltenes, along with a greater consumption of hydrogen from hydrogen donors.

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REFERENCES

1. Burke, D. P., Chem. Week, Vol. 115, No. 11, pp 38-43, 1974.
2. Klass, D. L., Chem. Tech., pp 499-510, July 1975.
3. Schmid, B. K., and H. Beuther, Ind. Eng. Chem., Proc. Res. Devel., Vol. 6, No. 2., pp 207-212, 1967.
4. Berti, V., C. Padovani, and F. Todesca, 6th World Petrol. Congr., Sect. III, Paper 8, Frankfort, 1963.
5. Kroenig, W., "The Catalytic Hydrogenation of Coal, Tar, and Petroleum," Springer-Verlag, Berlin, 1950, pp 79, 80.
6. Vlugter, J. C., and P. Van't Spijker, 8th World Petrol. Congr., PD 12, Paper 5, Moscow, 1971.
7. Given, P. H., D. C. Cronauer, W. Spackman, H. L. Lovell, A. Davis, and B. Biswas, Fuel, Vol. 54, No. 1, pp 34-39, 1975.
8. Kovach, S. M. and J. Bennett, 169th National Meeting, ACS, Div. Fuel Chemistry, Preprints, Vol. 20, No. 1, pp 143-169, 1975.
9. Akhtar, S., S. Friedman, and P. M. Yavorsky, U.S. BuMines TPR 35, July 1971, 11 pp.
10. Haensel, V., E. L. Pollitzer, and C. H. Watkins, 6th World Petrol. Congr., Sect. III, Paper 17, Frankfort, 1963.
11. Karr, C., Jr., J. O. Mapstone, Jr., L. R. Little, Jr., R. E. Lynch, and J. R. Comberiati, Ind. Eng. Chem., Product Res. Devel., Vol. 10, No. 2, pp 204-208, 1971.
12. Brahmachari, B. B., M. R. Saha, P. B. Choudhury, and A. K. Ganguli, Proc. Symp. Chem. Oil Coal 1969, pp 170-174, 1972.
13. Karr, C., Jr., J. R. Comberiati, K. B. McCaskill, and P. A. Estep, J. Appl. Chem., Vol. 16, No. 1, pp 22-27, 1966.

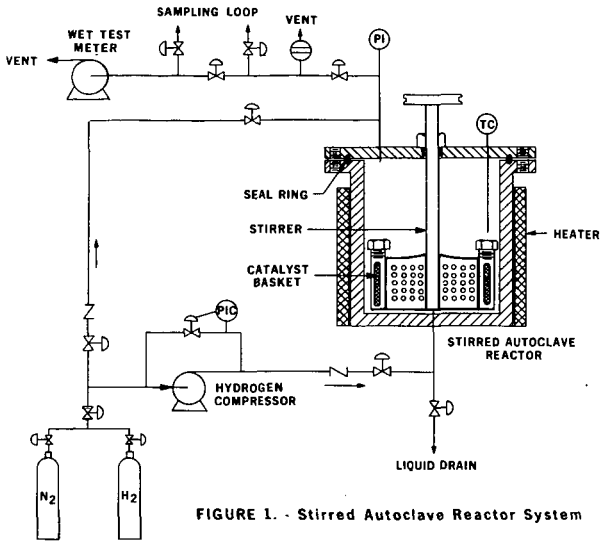

FIGURE 1. - Stirred Autoclave Reactor System

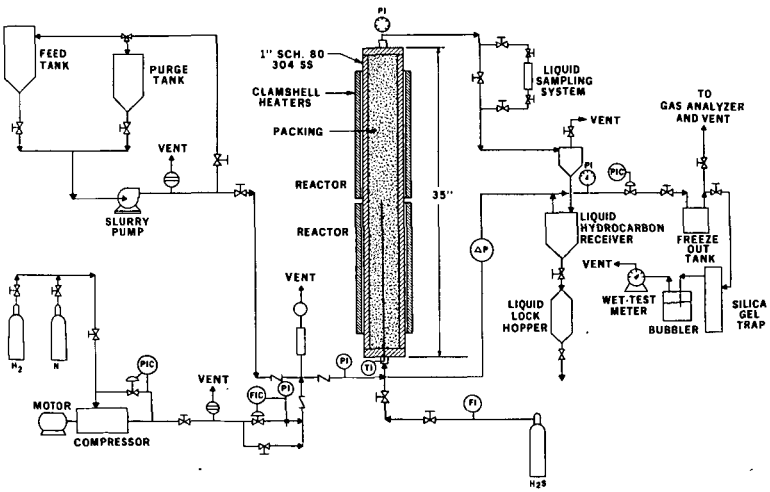

FIGURE 2. - Laboratory-Scale Flow System

Table 1. - Mass Balance for Stirred Batch Reactor Runs

Run conditions	Grams In				Grams Out							Ratio total grams out, total grams in
	Coal	Hydrogenated oil or 1st stage product	H_2 gas	Total	Liquid product	Tars [1]	Monitored gases [2]	Unmonitored components [3] NH_4	H_2S	H_2O	Total	
First-step [4] Denstone extreme	298.70	597.30	24.24	920.20	792.10	5.45	82.08	0.19	15.69	20.89	916.40	0.9959
First-step [5] Denstone mild	601.30	1202.70	26.45	1830.45	1673.69	16.90	53.27	-1.12	20.51	35.83	1798.99	0.9828
First-step [4] alpha-alumina extreme	307.67	612.33	19.41	939.41	791.70	24.50	78.41	-0.12	12.80	21.79	929.08	0.9890
First-step [5] alpha-alumina mild	599.20	1198.60	13.22	1811.02	1635.90	23.15	64.31	-3.14	21.83	36.89	1778.94	0.9823
Second-step [6] Denstone extreme	---	233.30	13.23	246.53	222.60	---	19.19	0.11	0.06	-0.04	241.92	0.9813
Second-step Denstone mild	---	233.00	13.23	246.23	209.50	---	15.98	0.22	0.43	0.79	226.92	0.9216
Second-step alpha-alumina extreme	---	222.00	13.22	235.22	198.20	---	12.70	1.00	0.22	0.45	212.57	0.9037
Second-step alpha-alumina mild	---	213.00	13.22	226.22	205.40	---	14.88	0.41	0.32	-0.08	220.93	0.9766

[1] Residual products sticking to equipment.
[2] Monitored gases: H_2, CO, CH_4, C_2H_6, CO_2, C_2H_4, C_3H_8, C_4H_{10} by gas chromatography.
[3] Unmonitored components: NH_3, H_2S, H_2O. Amounts of these components were calculated from the differences between input and output N, S, and O.
[4] Hydropyrolytic first-step with Denstone vitreous ceramic packing, at 1,800 psig and 450° C.
[5] 1,500 psig, 430° C.
[6] All four second-step runs with the cobalt molybdate catalyst, at 1,500 psig and 380° C, using unfiltered first-step product as feed.

Table 2. - Hydrogen Balances for Stirred Batch Reactor Runs

Run conditions	Grams H_2 In				Grams H_2 Out					Ratio, total grams out, / total grams in	Grams, H_2 gas in, corrected
	Coal	Hydrogenated oil or 1st stage product	H_2 gas	Total	Liquid product	Tars[1]	Monitored gases[2]	Unmonitored components[3]	Total		
First-step[4] Denstone extreme	12.90	41.81	24.25	78.96	55.45	0.22	18.98	3.27	77.92	0.9868	23.21
First-step[5] Denstone mild	25.98	84.19	26.45	136.62	112.13	0.68	12.90	5.19	130.90	0.9581	20.73
First-step[4] alpha-alumina extreme	13.29	42.86	19.41	75.56	54.23	1.47	19.31	3.17	78.18	1.0347	22.03
First-step[5] alpha-alumina mild	25.89	83.90	13.22	123.01	113.04	0.92	14.28	5.38	133.62	1.0863	23.44
Second-step[6] Denstone extreme	---	16.33	13.22	29.55	16.03	--	13.51	0.02	29.56	1.0003	13.23
Second-step Denstone mild	---	15.61	13.22	28.83	15.21	--	14.56	0.16	29.93	1.0382	14.32
Second-step alpha-alumina extreme	---	15.21	13.22	28.43	13.81	--	12.54	0.24	26.59	0.9353	11.38
Second-step alpha-alumina mild	---	14.72	13.22	27.94	14.17	--	14.64	0.09	28.90	1.0344	14.18

[1]Residual products sticking to equipment.
[2]Monitored gases: CH_4, C_2H_6, C_2H_4, C_3H_8, C_4H_{10} by gas chromatography.
[3]Unmonitored components: NH_3, H_2S, and H_2O. Amounts of H_2 consumed by forming these components were calculated from the difference between input and output N, S, and O.
[4]*Hydropyrolytic first-step with* Denstone vitreous ceramic packing, at 1,800 psig and 450° C.
[5]1,500 psig, 430° C.
[6]All four second-step runs with the cobalt molybdate catalyst at 1,500 psig and 380° C, using unfiltered first-step product as feed.

Table 3. - Carbon Balances for Stirred Batch Reactor Runs

Run conditions	Grams C In			Grams C Out				Ratio, total grams out, total grams in
	Coal	Hydrogenated oil or 1st stage product	Total	Liquid product	Tars[1]	Monitored gases[2]	Total	
First-step[3] Denstone extreme	180.33	539.36	719.69	706.71	5.18	54.21	766.10	1.0645
First-step[4] Denstone mild	363.01	1086.04	1449.04	1496.65	16.06	36.23	1548.94	1.0689
First-step[3] alpha-alumina extreme	185.74	552.93	748.67	707.46	22.05	52.46	781.97	1.0445
First-step[4] alpha-alumina mild	361.74	1082.34	1441.18	1463.64	21.99	44.97	1530.60	1.0599
Second-step[5] Denstone extreme	---	208.15	208.15	200.36	--	5.61	205.97	0.9895
Second-step Denstone mild	---	208.12	208.12	187.50	--	1.04	188.54	0.9059
Second-step alpha-alumina extreme	---	198.38	198.38	179.39	--	0.13	179.52	0.9049
Second-step alpha-alumina mild	---	190.57	190.57	184.80	--	0.19	184.99	0.9707

[1]Residual products sticking to equipment.
[2]Monitored gases: CO, CH_4, C_2H_6, CO_2, C_2H_4, C_3H_8, C_4H_{10} by gas chromatography.
[3]Hydropyrolytic first-step with Denstone vitreous ceramic packing, at 1,800 psig and 450° C.
[4]1,500 psig, 430° C.
[5]All four second-step runs with the cobalt molybdate catalyst at 1,500 psig and 380° C, using unfiltered first-step product as feed.

Table 4. - Solvent Extraction Analysis of Product from Two-Step Coal Liquefaction in Stirred Batch Reactor

First-step run conditions[1]	Weight percent							
	1,800 psig, 450°C, 3 hrs				1,500 psig, 430°C, 3 hrs			
Mineral residue	Not filtered between steps		Filtered		Not filtered between steps		Filtered	
First-step reactor material	Denstone	Alpha-alumina	Denstone	Alpha-alumina	Denstone	Alpha-alumina	Denstone	Alpha-alumina
Fraction								
Benzene insolubles	11.3	11.5	9.2	10.5	12.3	14.4	15.0	18.6
Asphaltenes (benzene-soluble, cyclohexane-insoluble)	9.3	5.2	26.1	11.6	16.3	14.4	26.0	16.5
Oils[2] (cyclohexane-soluble)	79.4	83.3	64.7	77.9	71.4	71.2	59.0	64.9

[1] Second-step run conditions of all eight runs: 1,500 psig, 380°C, 1 hr, presulfided cobalt-molybdenum on silica-promoted alumina.

[2] Includes the bulk of the oil used to make up the coal/oil slurry (ratio 1:2).

Table 5. - Coal-Derived Compounds and Alkylated Compounds in Two-Step Products, Using Filtered Feed for Second-Step

First-step run conditions	Weight percent[1]			
	1,800 psig, 450°C		1,500 psig, 430°C	
First-step reactor material	Denstone	Alpha-alumina	Denstone	Alpha-alumina
Trimethylbenzenes	0.40	0.40	0.23	0.08
Methyl-, Dimethyl-, and Ethylnaphthalenes	11.58	14.04	9.95	9.73
Methylbiphenyls	0.43	0.44	0.32	0.37
Methyldibenzofurans	3.10	2.91	2.71	3.65
Methylfluorenes[2]	1.07	1.16	0.85	1.40
Methylphenanthrenes	2.60	2.92	2.79	2.93
Methylpyrenes	0.45	0.50	0.35	0.54
Benz(c)phenanthrene[2]	0.10	0.14	0.18	0.37
Methylchrysene[2]	0.18	0.42	0.09	0.23
Benz(b,j,k)fluoranthene[2]	0.19	0.53	0.29	0.40
Benz(a & e) pyrene[2]	0.11	0.17	0.20	0.25
Methylbenz(a & e)pyrene[2]	0.04	0.07	0.04	0.06
Total coal-derived compounds	1.69	2.49	1.65	2.71
Percent Increase[3]		47.3		64.3
Total alkylated compounds	20.54	22.86	17.33	18.99
Percent Increase		11.3		9.6

[1] Calculated on the basis of the oil in the coal/oil slurry.
[2] Compounds not detected in the hydrogenated tar oil used for slurry, hence derived from coal.
[3] Percent increase in going from Denstone to alpha-alumina packing.

Table 6. - First-Step Hydrocarbon Gas Yields

Run conditions	Scf/lb coal			
	1,800 psig, 450°C		1,500 psig, 430°C	
Reactor material	Denstone	Alpha-alumina	Denstone	Alpha-alumina
Methane	1.645	1.890	0.835	0.985
Ethane	0.619	0.810	0.246	0.308
Propane	0.274	0.449	0.131	0.188
Butanes	0.043	0.070	0.022	0.025
Total	2.581	3.219	1.234	1.506
Percent increase	24.7		22.2	

Table 7. - Elemental Analysis of Two-Step Products, Using Unfiltered Feed for Second Step

First-step run conditions	Atomic H/C			
	1,800 psig, 450°C		1,500 psig, 430°C	
First-step reactor material	Denstone	Alpha-alumina	Denstone	Alpha-alumina
Benzene insolubles	0.62	0.65	0.72	0.73
Asphaltenes	0.64	0.70	0.75	0.78
Oils	0.95	0.94	0.95	0.99

Table 8. - Hydrogen Donors in Hydrogenated Tar Oil for Slurry Before and After Reaction with Coal: Analysis of First-Step Products

Type reactor	Weight percent					
	Batch			Flow		
Reactor conditions	1,800 psig, 450°C			1,500 psig, 440°C		
Reactor packing		Denstone	Alpha-alumina		Silica	Alpha-alumina
Hydrogenated tar oil	Lot A			Lot B-F		
Compound						
Indan	1.22	1.51	1.25	1.63	0.72	0.83
Methylindans	0.35	2.94	2.59	0.40	0.32	0.60
Tetralin	7.34	6.61	4.62	9.11	6.58	6.37
Methyltetralins	1.93	2.09	1.00	4.29	3.87	3.35
Dihydrophenanthene	3.08	1.32	1.11	2.00	1.28	1.17
Octahydrophenanthrene	---	---	---	2.04	1.66	1.89
Tetrahydrophenanthrene	2.42	1.18	1.12	4.30	4.09	2.92
Tetrahydropyrene	3.27	0.59	0.84	2.11	0.44	0.45
Hexahydropyrene	---	---	---	0.20	0.12	0.12
Dihydropyrene	0.97	0.60	0.69	0.80	0.40	0.40
Total	20.58	16.84	13.22	26.88	19.48	18.10
Percent reacted		18.2	35.8		27.5	32.6

Table 9. - Distillation of Slurry Vehicle Oils Compared With Distillation of Filtered First-Step Products from Stirred Batch Reactor Runs

Reactor conditions	Weight percent[1]					
	1,800 psig, 450°C			1,500 psig, 430°C		
Reactor packing		Denstone	Alpha-alumina		Denstone	Alpha-alumina
Hydrogenated tar oil	Lot A			Lot B		
Distillate range, °C						
40-202 (gasoline)	10.9	17.1	21.0	13.8	11.1	12.2
202-265 (kerosine)	34.0	27.9	28.4	32.5	28.1	26.7
265-340 (diesel oil)	40.9	39.7	33.1	40.6	40.3	41.4
340-392 (fuel oil)	13.1	12.5	13.9	12.0	15.9	16.2
392-495 (heavy oil)	1.1	2.8	3.6	1.1	4.6	3.5

[1] Based on distillation curve to FBP 495°C.

Table 10. - 0.2 Lb Coal/Hr Flow System

Reactor	First-Step		Second-Step	
Packing	Alpha-alumina	Silica	Co/Mo on SiO_2/Al_2O_3	
Reactor vol., ml	270	270	270[1]	270[2]
Temp., °C	440	440	380	380
Press., psig	1,500	1,500	1,500	1,500
H_2, scfh	7	7	7	7
Feed, g/hr	246	374	250	350
Coal/oil ratio	1:3	1:3	---	---
Run time, hrs	15.75	15.75	10.5	6.08
		Product Analysis		
Filter residue, pct.	3.64	5.55	---	---
Calcd. ash, pct.	4.88	4.88	---	---
Coal dissolved, pct.	100	97	---	---
	Filtered		As received	
Benzene insolubles, %	5.1	12.4	4.5	4.4
Asphaltenes, pct.	10.6	12.4	2.3	7.7
Oil, pct.	84.3	75.2	93.2	87.9
	Hydrocarbon Gas Yields, scf/lb Coal			
Methane	0.638	0.140	0.025	0.189
Ethane	0.150	0.043	0.017	0.041
Propane	0.047	0.018	0.025	0.038
Butanes	0.023	0.006	0.005	0.002
TOTAL	0.858	0.207	0.072	0.268

[1] Filtered product from alpha-alumina run as feed.
[2] Filtered product from silica run as feed.

Table 11. - Coal-Derived Compounds and Alkylated Compounds in First-Step Product from Flow System First-Step Reactor

	Weight percent[1]	
First-step packing	alpha-alumina	silica
Trimethylbenzenes	0.33	0.15
Methyl-, Dimethyl-, and Ethylnaphthalenes	12.98	13.09
Methylbiphenyls	1.29	1.16
Methyl- and Dimethyldibenzofurans	4.97	3.95
Methylfluorenes[2]	0.30	0.25
Methyl- and Dimethylphenanthrenes	3.60	3.21
Methylpyrenes[2]	0.55	0.94
Benz(c)phenanthrene[2]	0.13	0.37
Methylchrysene[2]	0.32	0.16
Benz(b,j,k)fluoranthene[2]	0.57	0.21
Benz(a&e)pyrene[2]	0.28	0.07
Methylbenz(a&e)pyrene[2]	0.09	0.00
Total coal-derived compounds	2.24	2.00
Total alkylated compounds	24.43	22.91

[1] Calculated on the basis of the oil in the coal/oil slurry.
[2] Compounds not detected in the hydrogenated tar oil used for slurry, hence derived from coal.

Table 12. - Densities of Slurry Vehicle Oils Compared With Densities of Filtered First-Step Products from Stirred Batch Reactor and Flow Reactor Runs

	Density, at 20°C					
Type reactor	Batch			Flow		
Reactor conditions	1,500 psig, 430°C			1,500 psig, 440°C		
Reactor packing		Denstone	Alpha-alumina		Silica	Alpha-alumina
Hydrogenated tar oil	Lot B			Lot B-F		
	1.0589	1.1000	1.0824	1.0056	1.1133	1.0600
Density increase		0.0411	0.0235		0.1077	0.0544

Table 13. - Elemental Analysis of Filtered First-Step Products from Batch and Flow Systems

	Elemental Weight Percents[1]					
Type reactor	Batch			Flow		
Reactor conditions	1,800 psig, 450°C			1,500 psig, 440°C		
Reactor packing		Denstone	Alpha-alumina		Silica	Alpha-alumina
Coal/oil slurry[2]	Lot A			Lot B-F		
Sulfur	1.70	0.37	0.30	1.29	0.16	0.37
Nitrogen	0.76	0.78	0.71	0.52	0.40	0.52
Oxygen	3.77	0.55	0.32	2.81	1.58	1.78
Carbon	86.38	90.98	92.17	87.03	90.05	89.91
Hydrogen	6.37	7.07	6.71	7.61	7.71	7.28
	98.98	99.75	100.21	99.26	99.90	99.86
Donors reacted[3]		18.2	35.8		27.5	32.6

[1] All elements by analysis.
[2] Moisture and ash free basis.
[3] Weight percent hydrogen donors reacted.

Table 14. - Flow System Second-Step Products,
Elemental Analyses, Weight Percent

Second-step			Cobalt molybdate	
Reactor conditions			1,500 psig, 380°C	
First-step packing			Silica	Alpha-alumina
Hydrogenated tar oil	Lot B-F			
Coal/oil slurry[1]		1:3		
Sulfur	0.09	1.29	0.20	0.13
Nitrogen	0.35	0.52	0.30	0.18
Percent decrease[2]			14.3	48.6
Oxygen	0.90	2.81	1.17	1.00
Hydrogen	8.18	7.61	8.44	8.97
Percent increase[2]			3.2	9.7
Carbon	90.03	87.03	89.56	89.53
Atomic H/C	1.09	1.05	1.13	1.20
Percent increase[2]			3.7	10.1

[1] Coal/hydrogenated tar oil, m.a.f. basis.
[2] Percent change of second-step product compared to hydrogenated tar oil.